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NOVEL NANOCOMPOSITE MEMBRANES FOR OSMOTICALLY DRIVEN PROCESSES: FABRICATION AND APPLICATION

by

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Certificate of Authorship

I, **Sungil Lim** declare that this thesis, is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney. This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution. This research is supported by the Australian Government Research Training Program.

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Abstract

For osmotically driven membrane processes, including forward osmosis (FO) and pressure retarded osmosis (PRO), water permeate was selectively induced across a semi-permeable polymeric membrane by the osmotic pressure generated from the salinity gradient. Although both FO and PRO processes are mainly driven by the osmotic pressure difference increased by the more concentrated draw solution on the permeate site of the membrane, membrane orientations for the processes are mainly confirmed as the active layer facing the feed solution (AL-FS) for FO, and the active layer facing the draw solution (AL-DS) for PRO, respectively. Although the AL-FS orientation for FO is beneficial for controlling membrane fouling on the dense active layer, diluted internal concentration polarisation (ICP) inside a FO membrane would be a major obstacle to maintaining the osmotic driving force under FO operation. These processes have been widely used for a variety of water treatments and hybrid systems as a low-energy process. However, the processes still have some critical challenges for membrane development, which are related to the following aspects: water permeability, reverse solute diffusion, concentration polarisation, membrane fouling and membrane stability. Although many earlier studies developed various kinds of polymeric membranes at laboratory scale to produce outstanding performances for overcoming existing challenges in FO and PRO processes, most of them never produced their own scaled-up membrane modules for commercial applications. This study, therefore, initially targeted novel nanocomposite membrane development for FO and PRO processes using the dual-blade casting technique and two hydrophilic nanomaterials (graphene oxide and halloysite nanotubes). Subsequently, we selected the best strategy in our activities, and the selected one was further investigated for its commercial viability.

A novel, thin-film composite (TFC) forward osmosis (FO) membrane with dual-layered substrate support was manufactured by a double-blade casting technique using different polysulfone (PSf) concentrations for top (15 wt%) and bottom (7 wt%) substrate layers. Graphene oxide (GO), at the optimum loading of 0.25 wt.%, was incorporated into the substrate layer, and the dual casting approach resulted in a membrane support with an extremely porous bottom structure and a dense top skin layer on which the polyamide active layer was effectively formed, which is desirable for reducing the internal concentration polarisation (ICP) so that the optimum dual-layered GO nanocomposite membrane exhibited high water permeability and good ion selectivity enhanced by the presence of well-dispersed hydrophilic GO in the PSf substrate. The optimum FO membrane with a fabric backing support exhibited similar FO performances to a fabric-free one under the same compositions, so that this approach presents positive potential for commercial application. In addition, the dual-blade casting technique was also benchmarked to develop high-performance PRO membranes. The approach incorporates halloysite nanotubes (HNTs) into the bottom polymer substrate layer and GO on the top layer substrate, on which a thin polyamide active layer is formed. The fabricated membrane substrate showed highly desirable membrane substrate properties, such as a high porosity, opened-bottom surface, suitable top-skin surface morphology for subsequent polyamide (PA) layer formation and high mechanical strength, which are all desirable for high-performance PRO processes. The bottom substrate incorporated with HNTs presented high fouling resistance and antibacterial properties due to the HNT's loading to a closed morphology, enhanced negative charge density and nano-sized pins on the bottom surfaces for alleviating the growth of microorganisms. The overall results of this study, therefore, suggested an alternative approach for developing outstanding PRO membranes with high performance, fouling resistance and antibacterial properties.

As the demand for new HF TFC membranes for FO increases, outer-selective hollow fibre (OSHF) TFC membranes were designed and developed by the novel approach used in this study. Thin and porous HF membrane substrates comprising a dense and smooth outer surface were manufactured by manipulating the air-gap distance in the HF fabricating unit. Subsequently, the vacuum-assisted interfacial polymerisation (VAIP) was specially modified for formation of a PA layer on the outer surface of the HF membrane substrate. The experimental results confirmed that the membrane substrate should be a smooth layer with a molecular weight cut-off (MWCO) of less than 88 kDa for subsequent PA layer formation via VAIP. The optimum OSHF TFC membranes manufactured using the air-gap (6 cm) exhibited outstanding FO performance. Furthermore, the optimised membrane demonstrated higher fouling resistance and cleaning efficiency using a silica-alginate spiked feed solution due to the membrane's physico-chemical characteristics. Moreover, large-scale membrane modules (22.8 cm^2) were successfully produced under our methodology, so that we can expect strong scalability of our membranes at a commercial scale.

For further development of the OSHF TFC membranes, specific hydrophilic nanomaterials were used to prepare OSHF thin-film nanocomposite (TFN) membranes. This study focused on size-controlled graphene oxide (SGO) and schiff base network-1 (SNW-1) as COF for the TFN membranes. The novel hypothesis and related mechanisms were demonstrated based on theoretical and experimental studies. Under the VAIP process, most SGO and SNW-1 nanofillers in meta-phenylenediamine (MPD) solution diffused on the membrane surface were horizontally stacked on the outer surface due to the vacuum suction from inside to outside, so that the nanofillers could be effectively embedded into the PA selective layer for producing OSHF TFN membranes with extremely low material loading. In particular, SGO nanosheets were ideally incorporated into the thin PA layer under the optimum loading at 0.0005 wt%, so that the produced TFN membranes exhibited extremely high levels

of water flux due to enhanced free volume and hydrophilicity of the PA composite layer from GO. In particular, SGO membranes exhibited better water flux and ion rejection than those of bulk GO embedded membranes (BGO) due to less water pathways and high free volume inside the PA layer from SGO's small lateral size. In addition, SGO demonstrated strong fouling resistance and high cleaning efficiency using artificial wastewater due to the loose accumulation of foulants on the surface. Using SNW-1 nanoparticles, high permeable OSHF TFN membranes were also successfully developed in this study. Based on the above mechanisms, SNW-1 nanoparticles were also securely incorporated into a PA layer with a less detrimental effect on the PA layer's integrity. It is expected that the secondary amine groups in SNW-1 may chemically react with the acyl chloride groups in the TMC solution through covalent bonding to further improve the integrity of the PA composite layer. As a result, the optimum OSHF TFN membranes exhibited the highest water transport and ion selectivity, which may be attributable to the porous structures and hydrophilic nature of SNW-1. In addition, SNW-1 nanoparticles were well organized inside the thin and dense PA matrix with retaining the PA layer's integrity. Accordingly, the optimum TFN membranes exhibited stable FO performances under long-term operation (72 hours), indicating that the SNW-1 embedded OSHF TFN membranes are able to possess strong durability under FO operation.

Accordingly, our approaches can be valuable and practical for producing superior FO and PRO membranes with outstanding performance and fouling resistance among existing research, and commercial TFC and TFN membranes for their applications. Through my discussion, it is expected that the OSHF TFN GO membranes (as stated in Chapter 6) can be the best performing FO membranes that this thesis has studied in terms of the membranes' intrinsic transport properties and fouling potential for water treatment. In addition, this OSHF TFN membrane makes it easier to scale up membrane modules for commercial application compared to that of the flat-sheet membrane. The scaled-up OSHF TFN membrane module can

also be a suitable candidate for various osmotically driven processes such as aerobic or anaerobic osmotic membrane bioreactors (OMBR), fertiliser-drawn OMBR (FD-OMBR) or high-turbidity water treatment. Furthermore, based on my dual-blade casting studies we may consider developing dual-layered OSHF TFC or TFN membranes for FO or PRO applications using a triple-orifice spinneret. Finally, we strongly believe that the proposed novel approaches can provide bright insights into advance of FO processes, and our research team is planning to scale up the optimum membrane modules for various process applications and their commercialisation in the near future.

Keywords: *membrane; forward osmosis; pressure retarded osmosis, thin film composite; thin film nanocomposite; dual blade casting; outer selective; flat-sheet; hollow fiber; graphene oxide; halloysite nanotubes; covalent organic framework*

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1. **Sungil Lim**, Myoung Jun Park, Sherub Phuntsho, Leonard D Tijing, Grace M Nisola, Wang-Geun Shim, Wook-Jin Chung, Ho Kyong Shon*, "Dual-layered nanocomposite substrate membrane based on polysulfone/graphene oxide for mitigating internal concentration polarization in forward osmosis", *Polymer* **110**, pp.36-48, 2017 **(Chapter 3)**

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